

# Overlapping of the characteristic regions in the decay on heterogeneous centers with equal number density

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The problem of the metastable phase decay has some specific solutions depended on the content of the condensating system. Namely, when the system contains only one type of heterogeneous centers one can successfully apply the iteration procedure [2]. When there are at least two types of heterogeneous centers all attempts to apply the iteration procedure [1] in the general situation fail. Then one has to consider the set of characteristic situations [3]. This case will be the subject of our analysis.

In some situations of the condensation process one can use the iteration procedure, but the reconsidered variant. In other situations one has to apply another theoretical approaches [3]. In [3] it was announced that the mentioned characteristic situations cover all variants of the possible external conditions (and the content of condensed system). The concrete proof is very long and dull and it is omitted in [3] due to lack of volume.

Ordinary the total number of heterogeneous centers is one and the same for all types of centers. For example, the total number of the positive ions is ordinary equal to the total number of the negative centers. This condition simplify the analysis and leads only to two characteristic situations.

These situations are quite analogous to those considered in the general situation [3]. Moreover, the way of proof is also quite analogous. That's why we restrict ourselves by the demonstration of the proof in this situation.

To formulate two characteristic situations we have to recall some definitions used in [3]. We shall start with fundamental characteristics of the condensation process. We shall mark by lower indexes  $+$  and  $-$  two types of

heterogeneous centers. In the real situation of ions these indexes can mark the positive and negative centers correspondingly. The absence of index means that the value can be referred to both types of heterogeneous centers.

To describe the first characteristic situation we denote by  $\Delta F$  the height of the activation barrier. Certainly it is the function of the supersaturation  $\zeta$  defined as

$$\zeta = \frac{n}{n_\infty} - 1$$

where  $n$  is the molecules number density of the vapor and  $n_\infty$  is the molecules number density of the saturated vapor. As far as we have two types of centers we have two values of the activation barrier heights  $\Delta_+ F$  and  $\Delta_- F$ .

The first characteristic situation is the situation of the "strong unsymmetry". It is characterized by the small value of parameter inverse to

$$\delta \Delta F \equiv |\Delta_+ F - \Delta_- F|$$

More rigorously speaking we have to mention that really the small value of parameter

$$\exp(-|\Delta_+ F - \Delta_- F|)$$

is required.

The second characteristic situation is the situation of the "moderate unsymmetry". To formulate it we have to introduce the values of

$$\Gamma \sim -\zeta \frac{d\Delta F}{d\zeta}$$

As far as there are two types of centers we have

$$\Gamma_+ \sim -\zeta \frac{d\Delta_+ F}{d\zeta}$$

and

$$\Gamma_- \sim -\zeta \frac{d\Delta_- F}{d\zeta}$$

The second characteristic is characterized by the small value of parameter

$$\delta_r \Gamma = \frac{|\Gamma_+ - \Gamma_-|}{\Gamma_+ + \Gamma_-}$$

Here we shall show that these two situations exhaust all possibilities. The structure of consideration is the following:

- In the first part we shall present general reasons which allow to hope that the mentioned situation can cover all possibilities of experimental conditions.
- In the second part we shall derive the required overlapping for several models of heterogeneous centers. This illustrates the proof and gives the answer in some limit situations which will be used later.
- In the third part we shall give the derivation of the statement for the case of ions. The way of derivation will be also spread to the general case.

All definitions from [3] are acceptable. We shall follow the system of units and definitions used in these papers.

## 1 General remarks

The difference between two types of heterogeneous centers is induced by some abstract charge  $q$ . In the situation of ions it is a real electric charge, in other situations it is the abstract charge.

Let us suppose that we can vary  $q$  starting from the zero value<sup>1</sup>. When  $q = 0$  we have  $\Delta_+ F = \Delta_- F$  and  $\Gamma_+ = \Gamma_-$ . When  $q$  is increasing then  $\delta_r \Gamma$  and  $\delta \Delta F$  are increasing also. Let us stop when

$$\delta \Delta F = 1 \tag{1}$$

We mark this value of  $q$  as  $q_h$ .

Having introduced parameter

$$\delta_r \Delta F \equiv \frac{\delta \Delta F}{\Delta_+ F + \Delta_- F}$$

one can note that

$$\delta_r \Delta F|_{q_h} \ll 1 \tag{2}$$

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<sup>1</sup>In the case of ions there is an elementary charge of an electron but we use this way only for a formal derivation.

The activation barrier height  $\Delta F$  can be presented as

$$\Delta F = \int_{\zeta}^{\zeta_0} \frac{\Gamma}{\zeta} d\zeta$$

where  $\zeta_0$  is the supersaturation when the activation barrier disappears. One can present the last integral as

$$\Delta F(\zeta) = \frac{\Gamma(\zeta')}{\zeta'} (\zeta_0 - \zeta)$$

where  $\zeta'$  is some value between  $\zeta$  and  $\zeta_0$ . Then

$$\Delta F = \frac{\Gamma(\zeta)}{\zeta} \Delta\zeta$$

where

$$\Delta\zeta \equiv (\zeta_0 - \zeta) \frac{\Gamma(\zeta')}{\Gamma(\zeta)} \frac{\zeta}{\zeta'}$$

The value  $\Delta\zeta$  has the sense of the characteristic distance from  $\zeta$  until the value where the essential activation barrier disappears in comparison with initial value (this value isn't  $\zeta_0$ ). The function  $(\zeta_0 - \zeta)/\Delta\zeta$  is a smooth function of  $\zeta$ .

Two types of heterogeneous centers induces two values  $\Delta_+\zeta$  and  $\Delta_-\zeta$ .

One can easily show that

$$\Delta_+\zeta|_{q < q_h} \approx \Delta_-\zeta|_{q < q_h} \quad (3)$$

We shall show the last estimate very qualitatively.

Really, the barrier character of condensation implies that

$$\Delta_+ F \gg 1$$

$$\Delta_- F \gg 1$$

This leads also to<sup>2</sup>

$$\frac{d\Delta_+ F}{d\zeta} = \frac{\Gamma_+}{\zeta} \gg 1$$

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<sup>2</sup>It is necessary for continuous description of the nearcritical region.

$$\frac{d\Delta_- F}{d\zeta} = \frac{\Gamma_-}{\zeta} \gg 1$$

Then the violence of the required condition leads to the violence of (1). So, one can now directly see (3).

One can keep in mind that the most sharp function of the supersaturation is  $\Gamma$  and the smooth functions are  $\Delta F$  and  $\Delta\zeta$ . Then it is reasonable to transform this picture into the dependence on  $q$ . Namely, one can consider that for the given supersaturation  $\zeta$  the value  $\Gamma$  is the sharp function of  $q$  and the values  $\Delta F$  and  $\Delta\zeta$  are more smooth functions. This can not be rigorously proven but seems to be a reliable qualitative picture. In the second section the similar facts will be justified for concrete types of heterogeneous centers.

The mentioned approximate coincidence of  $\Delta_+\zeta$  and  $\Delta_-\zeta$  allows to introduce

$$\Delta\zeta \equiv \frac{1}{2}(\Delta_+\zeta + \Delta_-\zeta)$$

and approximately substitute  $\Delta_+\zeta$  and  $\Delta_-\zeta$  by  $\Delta\zeta$ .

Then one can rather approximately show that

$$|\Delta_+ F - \Delta_- F| \approx \left| \frac{\Gamma_+}{\zeta_+} - \frac{\Gamma_-}{\zeta_-} \right| \Delta\zeta \quad (4)$$

and as far as

$$\Delta\zeta/\zeta \ll 1$$

one can come to

$$\left| \frac{\Gamma_+}{\zeta_+} - \frac{\Gamma_-}{\zeta_-} \right| \Delta\zeta \approx \frac{|\Gamma_+ - \Gamma_-|}{\zeta_p} \Delta\zeta$$

where  $\zeta_p = (\zeta_+ + \zeta_-)/2$ . In the last relation one can take as  $\zeta_p$  approximately both  $\zeta_+$  and  $\zeta_-$  with a rather small relative error.

Now one can express  $\Delta\zeta$  through  $\Delta F$  and substitute it into the last relation. Then it comes to

$$|\Delta F_+ - \Delta F_-| \approx \frac{|\Gamma_+ - \Gamma_-|}{\zeta_p} \frac{\zeta_p \Delta_\pm F}{\Gamma_\pm} = \frac{|\Gamma_+ - \Gamma_-|}{\Gamma_\pm} \Delta_\pm F$$

The last estimate solves the problem of overlapping of the mentioned regions. Really, as far as  $\Delta_\pm F \gg 1$  we see that at  $q_h$  where  $|\Delta_+ F - \Delta_- F| \sim 1$  the small value  $|\Gamma_+ - \Gamma_-|/\Gamma_\pm$  is guaranteed.

We have to note that the validity of (4) is the matter of question. Certainly, one can adopt  $\Delta_{\pm}F \sim \Gamma_{\pm} \frac{\Delta\zeta}{\zeta}$ , but when we coming to the difference  $\Gamma_+ - \Gamma_-$  the relative error increases many times. This disadvantage leads to some further remarks.

## 2 Model systems

Here we shall consider three simple models and show the necessary overlapping directly. This will illustrate that the overlapping of the regions  $|\Delta_+F - \Delta_-F| \geq 1$  and  $\delta_r\Gamma \ll 1$  is rather natural.

### 2.1 Pseudo homogeneous model

Suppose that  $R_{c+} = R_{c-} = R_{c\ q=0}$  where  $R$  is the radius of the embryo, index "c" denotes the critical embryo. This corresponds to the weak influence of the nuclei on the surface region of the nearcritical embryo. Later we shall approximately suppose that  $\nu_{c+} = \nu_{c-} = \nu_{c\ hom}$  where  $\nu$  is the number of the molecules inside the embryo and index *hom* corresponds to the homogeneously formed embryo.

Later the index *hom* differs from the subscript  $q = 0$  (Index "q=0" supposes only that the terms depended on the sign of the charge are put to zero. All other terms depended on the absolute sign of the charge are conserved.) The role of the terms depended on the sign of a charge is rather small in comparison with the role of the terms depended on the absolute value of a charge<sup>3</sup>. So, one can use the decomposition starting from  $q = 0$  when all terms independent on the charge sign taken directly into account.

Now we shall return to direct calculations. For  $\Gamma_+$  and  $\Gamma_-$  we have

$$\Gamma_+ \sim \nu_{hom} - \nu_{e+}$$

$$\Gamma_- \sim \nu_{hom} - \nu_{e-}$$

Then

$$\frac{\Gamma_+ - \Gamma_-}{\Gamma_{\pm}} = \frac{\nu_{e-} - \nu_{e+}}{\nu_{hom} - \nu_{e\pm}}$$

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<sup>3</sup>The homogeneous nucleation rate isn't between the rates of embryos formation on the "positive" and "negative" heterogeneous centers. Both positive and negative centers are the active centers of the condensation.

For  $|\Delta_+ F - \Delta_- F|$  we have a very rough estimate

$$|\Delta_+ F - \Delta_- F| \sim F_-(\nu_{e-}) - F_+(\nu_{e+})$$

All dependence on sign is in the last difference. We have to estimate the last difference by the smoothest dependence. Let us take the homogeneous dependence for this value. Then

$$F_-(\nu_{e-}) - F_+(\nu_{e+}) \sim \frac{a}{3}(\nu_{e+}^{2/3} - \nu_{e-}^{2/3}) \equiv p$$

where  $a$  is the renormalized surface tension.

Having estimated  $\nu_{hom} - \nu_{e\pm} > k\nu_{e\pm}$  with some parameter  $k$  close to 1 one can use for  $(\Gamma_+ - \Gamma_-)/\Gamma_{\pm}$  very rough (and smooth) estimate

$$\frac{\Gamma_+ - \Gamma_-}{\Gamma_{\pm}} < \frac{\nu_{e-} - \nu_{e+}}{k\nu_{e\pm}} \equiv \delta$$

If  $\delta$  is small then

$$p = \frac{a}{3}(\nu_{e+}^{2/3}(1 - (1 - k\delta)^{2/3})) \approx A\delta k$$

where

$$A \equiv \frac{a}{3} \frac{2}{3} \nu_{e+}^{2/3} \gg 1$$

The property  $Ak \gg 1$  guarantees that the regions  $\delta \ll 1$  and  $p \geq 1$  are overlapped.

## 2.2 Linear approximation model

We shall start from the rigorous formula

$$\Gamma_{\pm} \sim \nu_{c\pm} - \nu_{e\pm}$$

When  $\zeta = \zeta_{0\pm}$  the difference in the r.h.s. goes to zero. Now we shall introduce approximation

$$\Gamma_{\pm} \sim \gamma_{\pm}(\zeta - \zeta_{0\pm})$$

which implies that the difference  $\nu_{c\pm} - \nu_{e\pm}$  is the linear function of the supersaturation. This approximation has to be valid at some effective supersaturations which makes the main contribution into the activation barrier

height<sup>4</sup>. As it will be seen in the next subsection this approximation isn't valid when  $\zeta$  is near  $\zeta_0$ .

Having integrated the suggested approximation we come to

$$\Delta_{\pm}F = \frac{\gamma_{\pm}}{2}(\zeta - \zeta_{0\pm})^2$$

For  $q = q_h$  we have

$$1 = \left| \frac{\gamma_+}{2}(\zeta - \zeta_{0+})^2 - \frac{\gamma_-}{2}(\zeta - \zeta_{0-})^2 \right|$$

or

$$1 = \Delta_+F \left| 1 - \frac{\gamma_-}{\gamma_+} \left( \frac{\zeta - \zeta_{0-}}{\zeta - \zeta_{0+}} \right)^2 \right|$$

The value  $(\zeta - \zeta_{0-})/(\zeta - \zeta_{0+})$  has to be close to 1 or it has to be  $\Delta_+F - \Delta_-F \sim \Delta_+F \gg 1$  which solves the situation.

Then

$$1 = \Delta_+F \left| 1 - \frac{\gamma_-}{\gamma_+} \right|$$

or

$$1 \gg (\Delta_+F)^{-1} = \left| 1 - \frac{\gamma_-}{\gamma_+} \right|$$

It can be valid only when

$$\left| 1 - \frac{\gamma_-}{\gamma_+} \right| \ll 1$$

One can see that

$$\left| 1 - \frac{\gamma_-}{\gamma_+} \right| \sim \left| \frac{\Gamma_+ - \Gamma_-}{\Gamma_{\pm}} \right|$$

So,

$$\left| \frac{\Gamma_+ - \Gamma_-}{\Gamma_{\pm}} \right| \ll 1$$

which shows the overlapping.

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<sup>4</sup>Due to  $\frac{d\Delta F}{d\zeta} \sim \zeta\Gamma$  one can imagine  $\Delta F$  as the result of growth of  $\Delta F(\zeta)$  where  $\zeta$  is falling from  $\zeta_0$  to  $\zeta$ .



## 2.3 Moderate behavior model

Now we shall construct the general model corresponding to the formation and disappearing of the metastable state. The simplest form of the free energy corresponding to the appearance of the gap in the region of the small sizes is following

$$F \sim -b(\nu - \nu_0) + c(\nu - \nu_0)^3$$

where  $\nu_0$  is the characteristic value<sup>5</sup>.

Here  $b$  plays the role of the chemical potential (or supersaturation) and  $c$  is some negative parameter associated with the nuclei and independent (weakly dependent) on the supersaturation.

Denoting  $\nu - \nu_0$  via  $x$  one can get

$$\begin{aligned} -x_e = x_c &= \left(\frac{b}{3|c|}\right)^{1/2} \\ \Delta F &= \frac{4}{3^{3/2}} \frac{b^{3/2}}{|c|^{1/2}} \\ \Gamma &\sim \frac{d\Delta F}{db} = 2x_0 = \nu_c - \nu_e \end{aligned}$$

which confirms  $\Gamma \sim \nu_c - \nu_e$  directly.

The value of  $b$  is the variable, the value of  $c$  is supposed to be parameter. Now it is clear that  $\Gamma_+$  essentially differs from  $\Gamma_-$  only when  $c_+$  essentially differs from  $c_-$ . But it means that  $\Delta_+ F \sim |c|^{-1/2}$  essentially differs from  $\Delta_- F$ . As far as  $\Delta_{\pm} F \gg 1$  we see that it means that  $|\Delta_+ F - \Delta_- F| \gg 1$ . So the overlapping here can be also observed.

## 3 Real systems

### 3.1 Ions

Now we shall investigate the case of ions. The free energy of the embryo formation on the electric charge  $q$  can be presented in leading terms as following

$$F = -b\nu + a\nu^{2/3} + c\nu^{1/3} + (c_2 + c_q)\nu^{-1/3}$$

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<sup>5</sup>Here we are interested only in behavior of  $F$  near  $\nu_0$  and the asymptotic behavior of  $F$  isn't essential (it is wrong).

where  $b$  is the excess of the chemical potential in a liquid phase,  $a$  is the renormalized surface tension,  $c$  and  $c_2$  are some coefficients depended on the absolute value of the nuclei charge,  $c_q$  is the coefficient proportional to the charge and, thus, depended on the sign of the charge.

It is more convenient to use instead of  $\nu$  the variable  $\rho \equiv \nu^{1/3}$  which leads to

$$F = -b\rho^3 + a\rho^2 + c\rho + (c_2 + c_q)\rho^{-1}$$

For the critical size one can get

$$-3b\rho^4 + 2a\rho^3 + c\rho^2 = c_2 + c_q$$

We shall present the critical characteristics in the following form

$$\nu_{c \pm} = \nu_{c 0} + \delta_{\pm}\nu_c$$

$$\nu_{e \pm} = \nu_{e 0} + \delta_{\pm}\nu_e$$

$$\rho_{c \pm} = \rho_{c 0} + \delta_{\pm}\rho_c$$

$$\rho_{e \pm} = \rho_{e 0} + \delta_{\pm}\rho_e$$

where index 0 marks the values when  $c_q = 0$  (but  $c$  and  $c_2$  are conserved).

For  $\rho_0$  (both for critical and equilibrium values) we have

$$-3b\rho_0^4 + 2a\rho_0^3 + c\rho_0^2 = c_2$$

Then for  $\delta\rho$  (here will be  $\delta_+\rho = -\delta\rho \equiv \delta\rho$  in the main order for both critical and equilibrium values) one can get

$$-3b(\rho_0 + \delta\rho)^4 + 2a(\rho_0 + \delta\rho)^3 + c(\rho_0 + \delta\rho)^2 = c_2 + c_q$$

and in the main order

$$\delta\rho = \frac{c_q}{-12b\rho_0^3 + 6a\rho_0^2 + 2c\rho_0}$$

For the critical value of the free energy one can get

$$F \approx F_0(\rho_0) + F_0''(\rho_0)\frac{\delta\rho^2}{2} + c_q(\rho_0 + \delta\rho)^{-1}$$

where

$$F_0 = -b\rho^3 + a\rho^2 + c\rho + c_2\rho^{-1}$$

$$F_0'' = -6b\rho + 2a + 2c_2\frac{1}{\rho_0^3}$$

Then one can come to

$$F_{c+} - F_{c-} = 2c_q\rho_{0c}^{-1}$$

$$F_{e+} - F_{e-} = 2c_q\rho_{0e}^{-1}$$

and

$$\Delta_+F - \Delta_-F = 2c_q\left(\frac{1}{\rho_{0c}} + \frac{1}{\rho_{0e}}\right)$$

Now we shall turn to get  $\Gamma = \nu_c - \nu_e$ . In the main order  $\Gamma_+ = \Gamma_- = \Gamma_0 = \nu_{c0} - \nu_{e0}$ . In the first order

$$\Gamma_{\pm} = \Gamma_0 \pm (3\rho_c^2\delta\rho_c - 3\rho_e^2\delta\rho_e)$$

and

$$\frac{\Gamma_+ - \Gamma_-}{\Gamma_0} = \frac{6\rho_c^2\delta\rho_c - 6\rho_e^2\delta\rho_e}{\rho_c^3 - \rho_e^3}$$

Then one can take for the last value the following estimate<sup>6</sup>

$$\frac{\Gamma_+ - \Gamma_-}{\Gamma_0} \sim \frac{6\delta\rho_c}{\rho_c}$$

When  $q \sim q_h$  we get

$$1 = 2c_q\left(\frac{1}{\rho_{0c}} - \frac{1}{\rho_{0e}}\right) \sim \frac{2c_q}{\rho_{0e}}$$

and we see that  $c_q \gg 1$ .

Then for  $\frac{\Gamma_+ - \Gamma_-}{\Gamma_0}$  we can find

$$\frac{\Gamma_+ - \Gamma_-}{\Gamma_0} \sim \frac{3\rho_{0e}}{\rho_{0c}V(\rho_{c0})}$$

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<sup>6</sup>If we take here  $\delta\rho_e$  instead  $\delta\rho_c$  all consideration can be repeated even in details. Then we have to take  $V = V(\rho_{e0}) \gg 1$ .

where function  $V$  is given by

$$V(\rho) = -12b\rho^3 + 6a\rho^2 + 2c\rho$$

As far as  $V(\rho_{c0}) \gg 1$  we see that

$$\frac{\Gamma_+ - \Gamma_-}{\Gamma_0} \ll 1$$

which proves the overlapping.

### 3.2 Generalization for the arbitrary system

Now we can use the last constructions to investigate more general situation.

Suppose we have  $F_+$ ,  $F_-$  and  $F_0$ . Then

$$F_{\pm} = F_0 + \delta_{\pm}F$$

For the critical and equilibrium values we have

$$\nu_{c,e \pm} = \nu_{c,e 0} + \delta_{\pm}\nu_{c,e}$$

To find  $\delta_{\pm}\nu_{c,e}$  one can use

$$\frac{dF_{\pm}}{d\nu} = 0$$

or

$$\frac{dF_0}{d\nu} + \frac{d\delta_{\pm}F}{d\nu} = 0$$

or

$$\frac{dF_0}{d\nu}|_{\nu=\nu_0} + \frac{d}{d\nu}\left(\frac{dF_0}{d\nu}\right)|_{\nu=\nu_0}(\nu - \nu_0) + \frac{d\delta_{\pm}F}{d\nu} = 0$$

which gives

$$\delta_{\pm}\nu_{c,e} = \frac{\frac{d\delta_{\pm}F}{d\nu}|_{\nu=\nu_{c,e 0}}}{\frac{d^2F_0}{d\nu^2}|_{\nu=\nu_{c,e 0}}}$$

Ordinary in the leading term  $\delta_{\pm}F = \pm\delta F$ . Then

$$\delta_{\pm}\nu_{c,e} = \pm \frac{\frac{d\delta F}{d\nu}|_{\nu=\nu_{c,e 0}}}{\frac{d^2F_0}{d\nu^2}|_{\nu=\nu_{c,e 0}}}$$

Now we shall find  $\Delta_+ F - \Delta_- F$ . For  $F(\nu_c)$  we get

$$F(\nu_c) = F_0(\nu_{c0}) + \frac{1}{2} \frac{d^2 F_0}{d\nu^2} \delta\nu_c^2 + \delta F|_{\nu=\nu_{0c}}$$

Then

$$F_{c+} - F_{c-} = \frac{1}{3} \frac{d^3 F_0}{d\nu^3} \delta\nu_c^3 + 2\delta F|_{\nu=\nu_{0c}}$$

and

$$\Delta_+ F - \Delta_- F = \frac{1}{3} \frac{d^3 F_0}{d\nu^3} \delta\nu_c^3 + 2\delta F|_{\nu=\nu_{0c}} + \dots|_{\nu=\nu_e}$$

The first term corresponds to the opportunity missed in the previous section. Here we shall consider it more correctly.

When  $q = q_h$  we get

$$1 = \frac{1}{3} \frac{d^3 F_0}{d\nu^3} \delta\nu_c^3 + 2\delta F|_{\nu=\nu_{0c}} + \dots|_{\nu=\nu_e}$$

or

$$\frac{1}{3} \frac{d^3 F_0}{d\nu^3} \left( \frac{d\delta F}{d\nu} \right)^3 + 2\delta F|_{\nu=\nu_0} + \dots|_{\nu=\nu_e} = 1 \quad (5)$$

To find  $\Gamma_{\pm}$  we shall use  $\Gamma \approx \nu_c - \nu_e$ . Then

$$\frac{\Gamma_+ - \Gamma_-}{\Gamma_0} = 2 \frac{\delta\nu_c - \delta\nu_e}{\nu_{c0} - \nu_{e0}}$$

and

$$\frac{\Gamma_+ - \Gamma_-}{\Gamma_0} \sim \frac{\delta\nu_c}{\nu_{c0} - \nu_{e0}}$$

For further analysis one can express  $\frac{d^2 F}{d\nu^2}$  in terms of the halfwidth  $\Delta_c \nu$  of the nearcritical region. Then

$$\frac{d^2 F}{d\nu^2} \sim \Delta_c \nu^{-2}$$

where  $\Delta_c \nu$  is the halfwidth of the nearcritical region. Then (5) transforms into

$$\frac{1}{3} \frac{d^3 F_0}{d\nu^3} \left( \frac{d\delta F}{d\nu} \right)^3 (\Delta_c \nu)^6 + 2\delta F|_{\nu=\nu_{0c}} + \dots|_{\nu=\nu_{0e}} \sim 1$$

One can easily prove that in the l.h.s. of last relation there is no compensation and get the estimates

$$\frac{1}{3} \frac{d^3 F_0}{d\nu^3} \left( \frac{d\delta F}{d\nu} \Big|_{\nu_0} \right)^3 (\Delta_c \nu)^6 \leq 1 \quad (6)$$

$$\delta F|_{\nu=\nu_0} \leq 1$$

Then as far as

$$\frac{\Gamma_+ - \Gamma_-}{\Gamma_0} = \frac{\frac{d\delta F}{d\nu} \Big|_{\nu_0} (\Delta_c \nu)^2}{\nu_c - \nu_e}$$

according<sup>7</sup> to (6) one can see that

$$\frac{\Gamma_+ - \Gamma_-}{\Gamma_0} \sim \frac{1}{\nu_c - \nu_e} \left( \frac{3}{\frac{d^3 F_0}{d\nu^3}} \right)^{1/3}$$

Having used the estimate

$$\frac{d^3 F_0}{d\nu^3} \sim \frac{d^3 F_{hom}}{d\nu^3} \sim a\nu^{-7/3}$$

one can get

$$\frac{|\Gamma_+ - \Gamma_-|}{\Gamma_0} \sim \frac{\nu_c^{7/9}}{\nu_c - \nu_e}$$

which solves the problem when the denominator isn't too small. But the small value of denominator is already investigated in the section "Moderate behavior model".

For  $\delta F \sim 1$  we have

$$\left| \frac{\Gamma_- - \Gamma_+}{\Gamma_0} \right| \sim \frac{\Delta_c \nu}{\nu_c - \nu_e} \alpha \Delta F \left( \frac{1}{\nu_c} - \frac{1}{\nu_e} \right)$$

which solves as far as here  $\delta F \sim 1$  the problem when  $\nu_c$  isn't very close to  $\nu_e$ . But this situation is already investigated in the section "Moderate behavior model".

The leading property which allows to justify all necessary estimates is the fundamental condition  $\nu_c \gg 1$  which is necessary for the thermodynamic description of the embryo.

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<sup>7</sup> If we choose another opportunity  $\delta F \sim 1$  then having adopted  $\delta F \sim c_q/\nu^{-\alpha}$  with some parameter  $\alpha$  we repeat the previous section.

## References

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